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***IN THE UNITED STATES PATENT AND TRADEMARK OFFICE***

TITLE:

Thallium-Free Metal Halide Fill for Discharge Lamps and  
Discharge Lamp Containing Same

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Thallium-Free Metal Halide Fill for Discharge Lamps and  
Discharge Lamp Containing Same

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TECHNICAL FIELD

This invention relates generally to metal halide fill  
chemistries for discharge lamps. More particularly, this  
invention relates to thallium-free metal halide fills for  
10 discharge lamps.

BACKGROUND OF THE INVENTION

Metal halide discharge lamps are favored for their high  
efficacies and high color rendering properties which result from  
15 the complex emission spectra generated by their rare-earth  
chemistries. Particularly desirable are low-wattage ceramic  
metal halide lamps which offer improved color rendering, color  
temperature, and efficacy over traditional quartz arc tube  
types. This is because ceramic arc tubes can operate at higher  
20 temperatures than their quartz counterparts and are less prone  
to react with the various metal halide chemistries. Like most  
metal halide lamps, ceramic lamps are typically designed to emit  
white light. This requires that the x,y color coordinates of  
the target emission lay on or near the blackbody radiator curve.  
25 Not only must the fill chemistry of the lamp be adjusted to  
achieve the targeted emission, but this must also be done while  
maintaining a high color rendering index (CRI) and high efficacy  
(lumens/watt, LPW).

30 Most commercial ceramic metal halide lamps contain a complex  
combination of metal halides, particularly iodides. In general,  
iodides are more favored than fluorides because of their lower  
reactivity and are more favored than chlorides or bromides  
because they tend to be less stable at higher temperatures.  
35 Thallium iodide is a common component which is mainly used to

adjust the (x,y) color coordinates so that they lay on the blackbody curve. For example, a commercial 4200K lamp may contain mercury plus a mixture of TlI, NaI, DyI<sub>3</sub>, HoI<sub>3</sub>, TmI<sub>3</sub>, and CaI<sub>2</sub>. While lamps that contain thallium operate well at their  
5 rated power, their photometric characteristics deteriorate when the lamps are dimmed. This is primarily because the vapor pressure of thallium iodide is much higher than the vapor pressures of the other fill components. As the lamp power is reduced, the operating temperature of the arc tube is lowered  
10 and the 535 nm thallium atomic emission line begins to dominate the emission spectrum of the lamp. The disproportionate increase in the thallium emission causes the lamps to attain higher color temperatures and shifts the x,y color coordinates significantly above the blackbody curve. As a result, the  
15 dimmed lamps acquire an undesirable greenish hue. Experiments have shown that the higher the percentage of thallium in the fill, the greater the green shift.

Another problem with thallium-containing fills is that small  
20 temperature variations ( $\pm 50^{\circ}\text{C}$ ) lead to large variations in the correlated color temperature (CCT). This is problematic because the fill chemistry must be re-optimized each time a new outer jacket or reflector is added even though the arc tube and desired color coordinates are identical. Thallium iodide also  
25 has been associated with a low power factor (PF) and higher re-ignition (RI) peaks in some metal halide lamps. A low power factor means a less efficient lamp-ballast system and large RI peaks can cause excessive wall blackening. And lastly, thallium has been prohibited from use in U.S. household products since  
30 1975.

#### SUMMARY OF THE INVENTION

It is an object of this invention to obviate the disadvantages of the prior art.

It is another object of this invention to provide a metal halide fill which does not contain thallium.

It is a further object of the invention to provide a thallium-free metal halide fill which can meet the requirements for commercially desirable lamps, particularly when dimmed to less than their rated power.

In one aspect, the thallium-free metal halide fill of this invention is comprised of mercury,  
sodium iodide,  
an alkaline earth iodide selected from calcium iodide, strontium iodide, barium iodide, or combinations thereof, and  
a rare-earth iodide selected from cerium iodide, dysprosium iodide, holmium iodide, thulium iodide, or combinations thereof;

wherein the molar ratio of sodium iodide to alkaline-earth iodide is from about 0.6 to about 11, the molar ratio of sodium iodide to rare-earth iodide is from about 0.5 to about 2.8, and the molar ratio of alkaline-earth iodide to rare-earth iodide is from about 0.1 to about 2.

In another aspect, the thallium-free metal halide fill of this invention comprises mercury and a mixture of metal halide salts, the mixture containing about 25 to about 55 mole percent sodium iodide, about 20 to about 50 mole percent of a rare-earth iodide selected from cerium iodide, dysprosium iodide, holmium iodide, thulium iodide, or combinations thereof, and about 5 to about 40 mole percent of an alkaline-earth iodide selected from calcium iodide, strontium iodide, barium iodide, or combinations thereof.

In yet another aspect of this invention, the thallium-free metal halide fill further contains lithium iodide in an amount up to about 30 mole percent of the total iodide content.

5 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional illustration of a ceramic metal halide arc tube.

Fig. 2 is an illustration of a ceramic metal halide lamp.

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Fig. 3 is a ternary graph of the relative mole fractions of sodium iodide, alkaline-earth iodides ( $\text{AEI}_2$ ), and rare-earth iodides ( $\text{REI}_3$ ) of several examples of the thallium-free metal halide fill of this invention.

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Fig. 4 is a chromaticity diagram that demonstrates the effect of dimming on the color coordinates of various ceramic metal halide lamps.

20 DETAILED DESCRIPTION OF THE INVENTION

For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims taken in conjunction with the above-described  
25 drawings.

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The thallium-free metal halide fill of this invention contains, in general, mercury and a mixture of metal halide salts comprised of (1) sodium iodide ( $\text{NaI}$ ), (2) an alkaline-earth  
30 iodide ( $\text{AEI}_2$ ) selected from calcium iodide, strontium iodide, barium iodide, or combinations thereof, and (3) a rare-earth iodide ( $\text{REI}_3$ ) selected from thulium iodide, dysprosium iodide, holmium iodide, cerium iodide, or combinations thereof. The relative proportions of the metal halide salts in the mixture  
35 are designed to yield commercially desirable lamp

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characteristics, e.g., color temperature, CRI, high efficacy. Preferably, the correlated color temperature (CCT) is within the range from about 4000K to about 5000K, the CRI is greater than about 80, and the efficacy is greater than about 80 LPW. In one  
5 embodiment, the molar ratio of sodium iodide to alkaline-earth iodide is from about 0.6 to about 11, the molar ratio of sodium iodide to rare-earth iodide is from about 0.5 to about 2.8, and the molar ratio of alkaline-earth iodide to rare-earth iodide is from about 0.1 to about 2. In a more preferred embodiment, the  
10 mixture of metal halide salts comprises about 25 to about 55 mole percent sodium iodide, about 5 to about 40 mole percent alkaline-earth iodide, and about 20 to about 50 mole percent rare-earth iodide. This may be represented by the region encompassed by the polygon shown in Fig. 3 which is a ternary  
15 graph of the relative mole fractions of NaI, AEI<sub>2</sub>, and REI<sub>3</sub> in the metal halide salt mixture. The fill may also contain lithium iodide in an amount up to about 30 mole percent of the total metal iodide content.

20 Fig. 1 is a cross-sectional illustration of a ceramic metal halide arc tube. The arc tube 1 is a two-piece design which is made by joining two identically molded ceramic halves in their green state and then subjecting the green piece to a high temperature sintering. The method of making the arc tube  
25 typically leaves a cosmetic seam 5 in the center of the arc tube where the two halves were mated. A more detailed description of a method of making this type of ceramic arc tube is described in U.S. Patent 6,620,272 which is incorporated herein by reference. The arc tube is usually composed of translucent polycrystalline  
30 alumina, although other ceramic materials may be used.

The arc tube has hemispherical end wells 17a, 17b and is commonly referred to as a bulgy shape. The bulgy shape is preferred because it provides a more uniform temperature  
35 distribution compared to right-cylinder shapes such as those

described in U.S. Patent Nos. 5,424,609 and 6,525,476. The bulgy-shaped arc tube has an axially symmetric body 6 which encloses a discharge chamber 12. Two opposed capillary tubes 2 extend outwardly from the body 6 along a central axis. In this 2-piece design, the capillary tubes have been integrally molded with the arc tube body. The discharge chamber 12 of the arc tube contains a buffer gas, e.g., 30 to 300 torr Xe or Ar, and a thallium-free metal halide fill 8 as described herein.

Electrode assemblies 14 are inserted into each capillary tube 2. One end of the electrode assemblies 14 protrudes out of the arc tube to provide an electrical connection. The tips of the electrode assemblies which extend into the discharge chamber are fitted with a tungsten coil 3 or other similar means for providing a point of attachment for the arc discharge. The electrode assemblies are sealed hermetically to the capillary tubes by a frit material 9 (preferably, a  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Dy}_2\text{O}_3$  frit). During lamp operation, the electrode assemblies act to conduct an electrical current from an external source of electrical power to the interior of the arc tube in order to form an electrical arc in the discharge chamber.

Fig. 2 is an illustration of a ceramic metal halide lamp. The arc tube 1 is connected at one end to leadwire 31 which is attached to frame 35 and at the other end to leadwire 36 which is attached to mounting post 43. Electric power is supplied to the lamp through screw base 40. The threaded portion 61 of screw base 40 is electrically connected to frame 35 through leadwire 51 which is connected to a second mounting post 44. Base contact 65 of screw base 40 is electrically isolated from the threaded portion 61 by insulator 60. Leadwire 32 provides an electrical connection between the base contact 65 and the mounting post 43. A UV-generating starting aid 39 is connected to mounting post 43. Leadwires 51 and 32 pass through and are sealed within glass stem 47. A glass outer envelope 30

surrounds the arc tube and its associated components and is sealed to stem 47 to provide a gas-tight environment.

Typically, the outer envelope is evacuated, although in some cases it may contain up to 400 torr of nitrogen gas. A getter  
5 strip 55 is used to reduce contamination of the envelope environment.

### EXAMPLES

- 10 Several 70-watt ceramic metal halide test lamps were made with bulgy-shaped ceramic arc tubes. The composition of each arc tube fill is given below and the lamp photometry results are provided in Table 1. The points representing the relative mole fractions of NaI, AEI<sub>2</sub>, and REI<sub>3</sub> in the arc tube fills of  
15 Examples 2-9 are plotted in Fig. 3.

#### Example 1 (control)

Arc tube fill (thallium-containing):

- 20 4.5 mg Hg, 9 mg metal halide mixture (23:38:12:9:9:9 molar ratio of NaI:CaI<sub>2</sub>:TlI:DyI<sub>3</sub>:HoI<sub>3</sub>:TmI<sub>3</sub>) and 260 torr argon.

NaI:AEI<sub>2</sub> molar ratio = 0.60;

NaI:REI<sub>3</sub> molar ratio = 0.85;

- 25 AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 1.4;

NaI:TlI molar ratio = 1.92.



Example 2

Arc tube fill:

4 mg Hg, 8.6 mg metal halide mixture (47:16:37 molar ratio of  
5 NaI:CaI<sub>2</sub>:DyI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 2.94;

NaI:REI<sub>3</sub> molar ratio = 1.27;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 0.43.

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Example 3

Arc Tube Fill:

4 mg Hg, 9.1 mg metal halide mixture (47.5:15:37.5 molar ratio  
15 of NaI:BaI<sub>2</sub>:DyI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 3.17;

NaI:REI<sub>3</sub> molar ratio = 1.27;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 0.40.

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Example 4

Arc tube fill:

4.5 mg Hg, 8.3 mg metal halide mixture (39:8:23:30 molar ratio  
25 of NaI:BaI<sub>2</sub>:LiI:TmI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 4.88;

NaI:REI<sub>3</sub> molar ratio = 1.3;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 0.27.

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Example 5

Arc tube fill:

4.0 mg Hg, 8.5 mg metal halide mixture (28:29:43 molar ratio of  
5 NaI:CaI<sub>2</sub>:TmI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 0.97;

NaI:REI<sub>3</sub> molar ratio = 0.65;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 0.67.

10

Example 6

Arc tube fill:

4 mg Hg, 9.3 mg metal halide mixture (39.7:22.9:7.8:29.6 molar  
15 ratio of NaI:LiI:BaI<sub>2</sub>:TmI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 5.1;

NaI:REI<sub>3</sub> molar ratio = 1.3;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 0.26.

20

Example 7

Arc tube fill:

4 mg Hg, 9.1 mg metal halide mixture (52:9:39 molar ratio of  
25 NaI:BaI<sub>2</sub>:TmI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 5.8;

NaI:REI<sub>3</sub> molar ratio = 1.3;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 0.23.

30

Example 8

Arc tube fill:

4 mg Hg, 9.0 mg metal halide mixture (40.4:16.1:18.5:25.1 molar  
5 ratio of NaI:BaI<sub>2</sub>:SrI<sub>2</sub>:TmI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 1.2;

NaI:REI<sub>3</sub> molar ratio = 1.6;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 1.4.

10

Example 9

Arc tube fill:

4.15 mg Hg, 9.2 mg metal halide mixture (47.6:9.3:36.0:7.1 molar  
15 ratio of NaI:BaI<sub>2</sub>:TmI<sub>3</sub>:CeI<sub>3</sub>) and 260 torr Ar.

NaI:AEI<sub>2</sub> molar ratio = 5.1;

NaI:REI<sub>3</sub> molar ratio = 1.1;

AEI<sub>2</sub>:REI<sub>3</sub> molar ratio = 0.22.

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Table 1 - Photometry Results

	Watts	Volts	Amps	x	y	CCT	CRI	Lumens	LPW
Example 1 (control)	70	82.9	1.03	0.3830	0.3912	4034	91	6226	89
Example 2	70	83.3	1.03	0.3528	0.3241	4541	90	6235	89
Example 3	70	82.0	1.05	0.3518	0.3296	4623	90	6214	88
Example 4	70	91.4	0.93	0.368	0.362	4253	87	6379	91
Example 5	71	77.4	1.08	0.3658	0.3571	4295	92	6959	98
Example 6	70	76.5	1.09	0.3668	0.3568	4257	89	5936	85
Example 7	70	94.6	0.92	0.3698	0.3679	4241	87	6955	99
Example 8	72	81.3	1.06	0.3770	0.3700	4045	85	6144	85
Example 9	70	83.4	1.02	0.3548	0.3698	4728	85	6964	100

At rated lamp power, the thallium-free lamps of this invention  
5 exhibit photometric characteristics (CCT, CRI, efficacy, and x,y  
color coordinates) which are similar to their thallium-  
containing counterparts. However, unlike their thallium-  
containing counterparts, the thallium-free lamps continue to  
exhibit desirable photometric characteristics when dimmed to  
10 less than their rated power. This behavior can be seen in the  
chromaticity diagram shown in Fig. 4. The color coordinates of  
several lamps from Table 1 were measured as lamp power was  
varied from about 110 watts to about 40 watts (from about 160%  
to about 60% of rated power). The points, shown in Fig. 4 for  
15 each dimming curve, represent approximately 10 watt intervals of  
lamp power, from 50 to 100 watts. The dimming curves for the  
thallium-free lamps (Examples 5-8) are located slightly below  
the black-body radiator curve (Planckian locus) meaning that the  
white light emitted by the lamps has a desirable, slightly  
20 pinkish tint. The dimming curve for the thallium-containing  
lamp (Example 1) is located above the black-body curve meaning  
that the emitted white light has a greenish tint. More

importantly, the portion of the dimming curves for the thallium-free lamps that corresponds to power values that are less than the lamps' rated power of 70W run generally parallel to the black-body curve (Planckian Locus). This means that as the  
5 thallium-free lamps are dimmed from their rated power any changes in the color of the emitted light are only minimally perceptive. The corresponding region of the dimming curve for the thallium-containing lamp however runs in a direction which is generally normal to the black-body curve towards increasing y  
10 values. This means that as the thallium-containing lamp is dimmed the emitted light becomes perceptively more and more green which is highly undesirable.

While there has been shown and described what are at the present  
15 considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.